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THE RÔLE OF INORGANIC AGENCIES IN THE DEPOSITION OF CALCIUM CARBONATE

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Organic agencies are doubtless the predominant occasion of the deposition of calcium carbonate, yet certain inorganic factors may not safely be left out of account. The mode of action of the former, which is in part a biological question, we shall not enter into, but we shall limit ourselves to a discussion of the effects producible by variation of certain inorganic factors which affect directly the solubility of calcium carbonate. The question of the concentration of calcium relative to the limiting saturation concentration of calcium carbonate under the particular conditions—in other words, the relative degree of saturation with respect to calcium carbonate—has not received adequate consideration; this is largely the consequence of faulty data and of contradictory and erroneous statements regarding the solubility of calcium carbonate under various conditions. It is our purpose to direct attention to the quantitative effect, as deduced from laboratory study, producible by variation of those factors which, by affecting directly the degree of solubility of calcium carbonate, induce its precipitation from a solution saturated with it; and to emphasize the fact that many of the points now ambiguous may be settled by means of systematic and accurate investigation

of a certain group of properties of sea-water, properties which, moreover, are of high importance in connection with certain biological problems. The mode of treatment is similar to that employed by Stieglitz,¹ who, at the instance of Chamberlin, carried out series of calculations to ascertain the proportion of CaCO_3 which one might expect to find in gypsum that had been deposited from solutions saturated with respect to both CaSO_4 and CaCO_3 at different partial pressures of CO_2 in the atmosphere in contact with the solution. The principles, therefore, are not new, though the point of view differs somewhat; and we now have the advantage of more extensive data than were available in 1907.

The data bearing on the solubility of pure calcite have been collated and discussed at length in two recent papers,² to which the reader desirous of fuller information on the chemical side is referred. As it would lead too far to discuss here all details of the solubility-product constant and of its mode of calculation, we shall give only the established conclusions which are pertinent to the present discussion, premising that a symbol inclosed within brackets represents the concentration (expressed in moles per liter) of that particular ionic or molecular species.

1. In a solution at a fixed temperature saturated with pure calcite, the solubility-product—i.e. $[\text{Ca}^{++}][\text{CO}_3^{=}]$, the product of the respective concentrations of calcium-ion and carbonate-ion—is a constant, independent of the proportion of free CO_2 in the solution and of the presence of other salts. This characteristic solubility-product constant is to be carefully distinguished from the solubility which, as ordinarily measured, is the concentration of *total* calcium in a solution in equilibrium with solid calcite; and this calcium is associated with bicarbonate and hydroxide (and with any other anion present, e.g., chloride or sulphate) as well as with carbonate—indeed, under ordinary atmospheric conditions but a small fraction of the total

¹ J. Stieglitz, "The Relations of Equilibrium between the Carbon Dioxide of the Atmosphere and the Calcium Sulphate, Calcium Carbonate, and Calcium Bicarbonate in Water Solutions in Contact with It," in "The Tidal and Other Problems," by T. C. Chamberlin *et al.*, *Carnegie Inst. Publ. No. 107* (1909).

² J. Johnston, *Jour. Am. Chem. Soc.*, XXXVII (1915), 2001, hereinafter designated for convenience as *op. cit.*; Johnston and Williamson, *ibid.*, XXXVIII (1916), 975.

calcium is ever associated with carbonate. The fact of the constancy of this solubility-product in presence of solid calcite¹ enables us to calculate, with all the accuracy required for the purposes of this paper, the solubility of calcite under any specified conditions, e.g., in presence of calcium-ion or carbonate-ion from whatever source derived, provided only that we can ascertain what these ionic concentrations actually are.

2. The concentration of H_2CO_3 ("free" CO_2) in solution is regulated by the partial pressure (P) or proportion of CO_2 in the layer of atmosphere in contact with the solution, and conversely; and, for a given value of P , it diminishes with rising temperature, since the absorption coefficient (solubility) of CO_2 diminishes.

3. At a given temperature the total solubility as usually measured—i.e., the total concentration of calcium in the solution—varies with the concentration of H_2CO_3 (hence with P), owing to the fact that the latter determines the proportion of carbonate-ion CO_3^{--} , hydrocarbonate-ion HCO_3^- , and hydroxide-ion OH^- in accordance with definite mathematical expressions; and since the product $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ remains constant $[\text{Ca}^{++}]$ must vary inversely as $[\text{CO}_3^{--}]$. The presence of other salts also affects this total solubility; so long as pure calcite is the stable solid phase in equilibrium with the solution, the magnitude of this effect is readily calculable, since the several concentrations always adjust themselves until the solubility-product $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ attains its characteristic value.

4. The solubility-product constant of calcite diminishes with rising temperature; it is not affected to an appreciable extent by change of *hydrostatic* pressure.

The mathematical expressions are given below:

$$\begin{aligned} [\text{H}_2\text{CO}_3] &= cP \\ [\text{Ca}^{++}] [\text{CO}_3^{--}] &= K_c \text{ (in presence of solid calcite)} \\ [\text{HCO}_3^-]^2 / [\text{CO}_3^{--}] &= l[\text{H}_2\text{CO}_3] = lcP \\ [\text{OH}^-]^2 / [\text{CO}_3^{--}] &= m / [\text{H}_2\text{CO}_3] = m / cP \end{aligned}$$

where c , K_c , l , and m are constants at any given temperature.² We may note, moreover, that the free CO_2 and the total CO_2 (i.e.,

¹ Similar remarks apply, *mutatis mutandis*, to impure calcite or to aragonite; to this point we revert later.

² For their values and significance, see Johnston, *op. cit.*, p. 2011.

$[H_2CO_3] + [CO_3^{2-}] + [HCO_3^-]$) determine $[OH^-]$, the degree of alkalinity (or acidity) of the solution; and that no change can be made in any one of these quantities without affecting each of the others.

Accordingly the solubility of calcite is significant only if the concentration of free CO_2 is controlled and measured, for changes in the latter, such as may easily occur, exert a large influence on the amount dissolved.¹ This is evident from Table I, which gives the solubility

TABLE I
SOLUBILITY OF CALCITE AT 16° FOR VARIOUS VALUES OF P

CO ₂ IN THE ATMOSPHERE EXPRESSED		FREE CO ₂ OR H ₂ CO ₃ IN SOLUTION, PARTS PER MILLION	SOLUBILITY OF CALCITE, PARTS CaCO ₃ PER MILLION
As Partial Pressure P	As Parts per 10,000 (by Volume)		
0.0001	1.0	0.18	44
.0002	2.0	.36	55
.00025	2.5	.45	59
.0003	3.0	.55	63
.00035	3.5	.64	66
.0004	4.0	.73	69
0.0005	5.0	0.90	75

at 16° for various values of P not far removed from the proportion normally present in the atmosphere (about 3 parts per 10,000). Calculation shows that except for very small partial pressures of CO_2 the calcium in solution is associated almost entirely with bicarbonate—thus even when P is only 0.0005, the proportion as carbonate is only about 2 per cent, whereas when P is 1.0, the proportion is less than 1 part in 30,000; nevertheless, carbonate is still the solid phase which separates out, an excellent example of the fact that it is the solubility relations and not the “affinity” relations in solution that determine which of the possible stable solid phases shall appear.

¹ Neglect of this factor or, in general, a failure to secure equilibrium conditions is responsible for erroneous statements in the literature. For instance, the solubility as given by Treadwell and Reuter (*Z. anorg. Chem.*, XVII [1898], 170) is not a real solubility at all; acceptance of their figure (238 parts per million) has led several writers astray. Cf. *op. cit.*, p. 2009. Thus on this basis J. C. Jones (*Science*, XX [1914], 829) concluded that the waters of the Lake Lahontan basin are only about one-twentieth saturated with $CaCO_3$.

The change of solubility with temperature, the proportion of CO_2 being constant, is evident from Table II, which contains values interpolated from the curve expressing the observations by Wells,¹ as well as the molar absorption-coefficient (c) of CO_2 and the calculated value (K'_c) at each temperature. There is a slight error involved in identifying K'_c with the solubility-product constant $[\text{Ca}^{++}] [\text{CO}_3^{--}]$ except at temperatures close to 18° , because in calculating K'_c we have—for lack of better knowledge—assumed that the ratio (nr) of the first to the second ionization-constant of H_2CO_3 is independent of the temperature; nevertheless, since these values of K'_c were obtained from actual measurements of solubility, they enable one to calculate² for any temperature up to 30° the solubility of calcite under any conditions of CO_2 pressure or salt-concentration.³

TABLE II
THE SOLUBILITY OF CALCITE UNDER ATMOSPHERIC CONDITIONS
($P=0.00032$), AND THE SOLUBILITY-PRODUCT CONSTANT
AT SEVERAL TEMPERATURES

Temperature t	Solubility of Calcite Parts CaCO_3 per Million	Molar Absorption Coefficient of CO_2 at t c	Solubility-Product Constant $K'_c \times 10^3$
0	81	0.0765	1.22
5	75	.0637	1.14
10	70	.0535	1.06
15	65	.0455	0.99
20	60	.0392	0.93
25	56	.0338	0.87
30	52	0.0297	0.81

From the foregoing it follows that in order to decide definitely if a natural water is saturated with respect to calcite one must know: (a) the concentration of free CO_2 in the water, (b) the temperature, (c) the concentrations of the other constituents present. Of these the third is the only one which has in general been satisfactorily ascertained, but it is only of subsidiary importance; experimental data on the two important factors are commonly either lacking or

¹ R. C. Wells, *Jour. Wash. Acad. Sci.*, V (1915), 617.

² For the mode of calculation see Johnston, *op. cit.*, p. 2011.

³ This holds only so long as *calcite* is the stable phase. If the salt-concentration is such that some other carbonate (e.g., a double carbonate) is the stable phase, the appropriate constant must be employed in place of that characteristic of calcite.

untrustworthy.¹ On the other hand, the concentration of free CO_2 in any water, at a given temperature, can be calculated by means of the known absorption coefficient of CO_2 , if the proportion of CO_2 in the atmosphere with which it has been in contact is known;² and as at the present time this proportion is usually close to 3 parts in 10,000 the corresponding solubility of calcite in natural waters should be close to the values given in Table II. Consideration of the published analyses³ from this standpoint leads to the conclusion that the surface layers of the warmer portions of the sea (in so far as they have been investigated), as well as many river waters,⁴ are substantially saturated with calcite. Murray,⁵ in adverting to this question, states the opinion that "the ocean as a whole remains just about saturated for calcium carbonate"; but this statement is without doubt too sweeping, except in the sense that the concentration of CaCO_3 throughout the ocean is probably as great as it is in the warm surface layers. But there is also more direct evidence. Thoulet⁶

¹ The titration methods which have usually been employed for the determination of free CO_2 —and to some extent of combined CO_2 —are altogether untrustworthy, since the results depend upon the amount of indicator added and upon other factors which have not been adequately controlled. This question is discussed at length in another paper (J. Johnston, *Jour. Am. Chem. Soc.*, XXXVIII [1916], 947). Cf. also Morgulis and Fuller, *Jour. Biol. Chem.* XXIV (1916), 31.

² With regard to the solubility of CO_2 in a sea-water see C. J. J. Fox, *Trans. Faraday Soc.*, V (1909), 68.

³ See F. W. Clarke, *Data of Geochemistry*; but especially a paper by E. Dubois, "The Amount of the Circulation of CaCO_3 and the Age of the Earth." (*Proc. Acad. Wetenschappen Amsterdam* [1901], pp. 43–62). Cohen and Raken (*ibid.* [1901], p. 63) have determined directly the solubility of CaCO_3 in an artificial sea-water at 15° and found about 55 parts per million; but their method of experiment is not unexceptionable and would tend to yield low results; they also conclude that this sea-water is saturated with CaCO_3 . Wells also (*Jour. Wash. Acad. Sci.*, V [1915], 621) points out that the amount of carbonate carried by the Mississippi River diminishes steadily as it flows southward, i.e., in the direction of rising temperature.

⁴ Indeed, the amount carried by many rivers is much in excess of the true solubility, indicating that some of it is in suspension. Where such a river reaches the sea, the salts cause the flocculation of this and any other suspended material, and in this way induce the formation of deposits there.

⁵ Murray and Hiort, *The Depths of the Ocean* (1912), p. 180.

⁶ J. Thoulet, "Etude bathylithologique des côtes du Golfe de Lyons," *Annales de l'Institut Océanographique*, IV, fasc. VII (1912), pp. 32–35.

studied silt grains taken from various parts of the Gulf of Lyons, and observed upon them films of calcium carbonate which had been precipitated during the process of sedimentation; this shows, therefore, that the water of the Gulf of Lyons is substantially saturated with CaCO_3 . Recent experiments of A. G. Mayer¹ show that the sea-water about the coast of Florida is likewise substantially saturated, for shells exposed to it for a year lost no significant weight. Moreover, the investigations of T. W. Vaughan² on coral reefs "show that submarine solution is not effective there [about Florida] as all the bays, sounds, and lagoons are being filled with sediment," a conclusion which accords "with the conclusions reached by numerous investigators in the Pacific, which are that the more or less continuous walls inclosing lagoons have been formed by constructional geologic processes and that lagoon channels and atoll lagoons are not due to submarine solution."

The evidence just presented leads us, therefore, to the opinion that the surface layers of the ocean, except in the polar regions and within currents of cold water—in other words, the warmer portions of the ocean water—are substantially saturated with CaCO_3 . We wish to point out specifically, however, that this belief cannot be regarded as established (or indeed disproved) until trustworthy determinations of the several quantities concerned have been made; indeed, to emphasize the necessity of such investigations is the prime purpose of this paper. But in this connection it may be remarked that a *permanent* deposit of limestone can hardly result unless (1) the *final* solution locally in contact with it is saturated, or (2) the precipitated carbonate is protected from the water by an organic tissue or otherwise, or (3) the process of deposition is rapid, in water circulating very slowly or not at all, under which conditions re-solution by diffusion is very slow.

In this paper, which is dealing primarily with the chemical arguments, it would be out of place to take up the geologic lines of evidence which indicate that the ocean as a whole is not saturated with CaCO_3 , for this point is not at issue; but we may fitly advert to the

¹ A. G. Mayer, *Proc. Nat. Acad.*, II (1916), 28.

² T. W. Vaughan, *Am. Jour. Sci.*, XLI (1916), 133. See also his earlier papers, especially in the *Year Books* of the Carnegie Institution of Washington.

chemical arguments which have been adduced in favor of this position. Thus Tolman writes:¹

As direct evidence that the ocean is not saturated with calcium acid carbonate, we find (1) of the many hundred bottles of the Challenger's samples of sea-water, from all depths and collected at all temperatures, kept several years, only one or two showed deposit of lime.² (2) Sea-shells from the bottom of the Pacific show corrosion and re-solution.³ The Pteropod shells are not found below fifteen hundred fathoms, and two thousand eight hundred fathoms is the limit for the globigerina ooze.⁴ (3) Thoulet found by actual experiment that sea-water will dissolve calcium carbonate from shells, corals, etc.⁵ (4) Usiglio, studying the evaporation of the Mediterranean water at Cette, found that no precipitate was formed until the specific gravity of the sea-water increased from 1.02, the specific gravity of the unevaporated water, to 1.0503, when the first precipitation begins, composed largely of calcium carbonate with ferric oxide.⁶

Let us now consider these arguments severally. (1) That samples of surface water did not deposit CaCO_3 on standing is not good evidence one way or the other unless conditions were carefully controlled, for change of temperature or of concentration of CO_2 would influence the result. (2) This shows, of course, that the lower (and colder) layers are not saturated; to this point we revert later. (3) Reference to Thoulet's paper shows that his work proves nothing as to the point in question, for neither the temperature nor the partial pressure of CO_2 was controlled. Indeed, he writes: "In the case of marble . . . and of coral, the loss [of weight] in sea-water was *negative*. This result arises from the fact that small algae appeared . . . the weight of which confuses the result." (4) This observation also is no proof, in view of the well-known fact that solutions of calcium carbonate exhibit a great tendency to supersaturation when no solid CaCO_3 is already present; therefore it shows only that, when the density was 1.05, the degree of supersaturation had become so great that precipitation took place. From

¹ C. F. Tolman, *Jour. Geol.*, VII (1899), 604.

² *Challenger Reports*, p. 221.

³ *Jour. Geol.*, I, 504.

⁴ *Challenger Reports*, p. 221.

⁵ *Comptes rend.*, CVIII, 753.

⁶ *Encycl. Brit.*, XXI, 229.

this discussion, then, it follows that three of these arguments are not conclusive as to the point at issue.

Let us now consider the modes in which CaCO_3 may be precipitated. We shall for convenience arrange them under three heads, which, however, cannot be sharply differentiated: (1) direct evaporation of the water; (2) through organic agencies; (3) change of conditions, especially of temperature and concentration of free CO_2 , these being the predominant inorganic factors.

1. *By direct evaporation.*—When natural waters evaporate, CaCO_3 is commonly (though not necessarily) the first substance to be deposited, and may be very largely precipitated before any of the other salts separate;¹ the more soluble salts, moreover, will tend to be leached out of such deposits. But since all such deposits are of obvious origin and of minor importance, they need not detain us further.

2. *Deposition through organic agencies.*—The agencies which come under this category are of the greatest importance and are predominantly responsible for the deep-sea deposits, yet little as to their mode of action can be definitely stated until more is known about the biologic processes involved. This question is altogether beyond the scope of this paper; we shall mention merely two established effects of organic agencies, reverting to them later: viz., the abstraction of free CO_2 from fresh water by growing plants,² and the production of ammonia in sea-water by decaying organisms or by bacteria.³ Both of these effects disturb the equilibrium in a solution originally saturated with CaCO_3 , the former by diminishing the concentration of H_2CO_3 , the latter by increasing the concentration

¹ Cf. Van't Hoff's *Ozeanische Salzablagerungen*.

² Various references to these effects are given in Clarke's *Data of Geochemistry* under "Limestone." See especially C. A. Davis, *Jour. Geol.*, VIII (1900), 485, 494; IX (1901), 491. According to Murray, the calcareous algae common in the warmer oceans no doubt secrete their skeletons in the same way. See also S. T. Powell, "Effect of Algae on Bicarbonates in Shallow Reservoirs," *Jour. Am. Waterworks Assoc.*, II (1915), 703.

³ This question has been discussed recently by G. H. Drew (*Carnegi Institution Publ. No. 182* [1914], p. 7), and by Kellerman and Smith (*Jour. Wash. Acad. Sci.*, IV [1914], 400), and so need not be treated here. Many decaying organisms and bacteria (as well as the respiration of animals) produce CO_2 , and to this extent they would act as an adverse influence on the deposition of CaCO_3 .

of $\text{CO}_3^{=}$ directly,¹ the net result in either case being the precipitation of an amount of CaCO_3 which could readily be calculated by means of the equilibrium equations if the amount of CO_2 abstracted, or of ammonia produced, were known. But by this we do not imply that an organism cannot secrete calcium carbonate except from a solution already saturated with it. Nevertheless the possibility is open that the effects just considered may sometimes be in reality examples of the changes in conditions to be next considered—that the organism may be merely the agency which localizes the process, the mechanism which occasions the precipitation. It may even be that certain bacteria are abundant where CaCO_3 is being precipitated because there they can easily secure material—particularly CO_2 —needed for their life-processes; on this basis they would be concomitants, rather than causes, of the deposition of the carbonate.

3. *Change of conditions.*—The important physico-chemical factors are temperature, and concentration of free CO_2 , of the water; in comparison with these two all other such factors are entirely subsidiary. As an illustration of the magnitude of the effect producible by change of these factors, a change in the proportion of CO_2 in the air in actual contact with the solution from 3.3 down to 3.0 parts per 10,000—a change² which may occur at the present time—of itself decreases the solubility from 65 to 63 parts per million, and so will cause the ultimate precipitation of the corresponding quantity of CaCO_3 from a solution already saturated with it. A similar amount will be deposited³ if the temperature of the saturated solution rises about 2° C., the proportion of CO_2 in the air remaining constant; under these circumstances the concentration of free CO_2 in the water falls, and its diminution is responsible for the larger part of the diminished

¹ The production of free ammonia causes an increase in the concentration of OH^- and therefore an increase in $[\text{CO}_3^{=}]$, since the quotient $[\text{OH}^-]^2/[\text{CO}_3^{=}]$ is constant when P is constant, in accordance with the equation already given. It may be noted that the production by the decaying organisms of an ammonium salt such as NH_4NO_3 or $(\text{NH}_4)_2\text{SO}_4$ would tend to increase the solubility of CaCO_3 and hence would not favor its deposition.

² The range of variation in the course of geologic time has in all probability been very much greater than this with correspondingly larger possible consequences.

³ This of course implies that supersaturation does not take place; but in the sea supersaturation is highly improbable by reason of the great abundance of appropriate nuclei always present.

solubility, since the diminution of the solubility-product constant of calcite with temperature is, as we have seen, proportionally less than that of the absorption coefficient of CO_2 .

The abstraction of CO_2 from a saturated solution results ultimately, then, in the deposition of CaCO_3 , no matter what the agency which abstracts the CO_2 . This agency may be a diminished proportion of CO_2 in the air, or a higher temperature, or both; or it may be organisms which make use of the CO_2 in their vital processes, or the production by bacterial action of ammonia, which indirectly achieves the same result; or, in short, it may be any way in which the concentration of CO_2 may possibly be diminished. Consequently, if the surface layers of the sea are saturated, as we believe they are, precipitation of CaCO_3 will be brought about wherever any of the foregoing agencies are operative.

In this connection two points which are the consequence of accepting erroneous chemical data are to be noted. Thus Davis¹ in his excellent work on marls has made a slight slip. He observed that on bubbling oxygen gas through a solution containing CaCO_3 the latter was precipitated, and he attributed this effect to a specific action of the oxygen; but any other gas would have produced the same effect, which was actually due to the sweeping out of the CO_2 from the solution. Nor is it necessary to consider, when ammonia is being produced, whether it appears as hydroxide or as carbonate, or whether there is a subsequent metathesis with calcium sulphate or chloride or some other reaction; in either case the net result can be predicted immediately from a consideration of the effect of the added substance upon the concentration of calcium-ion and of carbonate-ion,² and of the magnitude of the product $[\text{Ca}^{++}] [\text{CO}_3^{=}]$ in relation to its precipitation value.³ To some this procedure may appear complicated; in reality, while it pays no heed to those easily derived arithmetical equations so often considered as representing reactions, it takes into account the several equilibria which must be adjusted,

¹ C. A. Davis, *Jour. Geol.*, VIII (1900), 487.

² Change of concentration of $\text{CO}_3^{=}$ affects, and is affected by, the concentration of HCO_3^- and OH^- , these being all dependent variables; see Johnston, *op. cit.*

³ Provided that calcite is still the stable solid phase in equilibrium with the solution; cf. footnote 3, p. 733.

and is the only procedure which will yield accurate results and lead to correct conclusions. Moreover, a comprehension of this question is desirable because this apparently complex equilibrium is typical of what takes place in many other systems, aqueo-igneous and igneous as well as aqueous; it is in but very few cases, however, that we know even what molecular species are important factors in the equilibrium, and in still fewer is any information available as to the quantitative relations at equilibrium.

There has, moreover, been considerable misapprehension as to the rôle of hydrostatic pressure in increasing the solubility of CaCO_3 ; thus in a recent paper Daly¹ writes: "On account of the higher temperatures and lower bottom pressures (*pressure increasing the solubility of the carbonate*) of the shallower water we should expect the rate of chemical precipitation of calcium carbonate at the bottom to be concentrated in the neritic (epicontinental) and shallower bathyal regions." And many similar statements relative to the effect of hydrostatic pressure might be quoted. As a matter of fact, the hydrostatic pressure² acting on the water is of itself an absolutely negligible factor; thus water a mile below the surface of the sea will hold in solution an amount of CaCO_3 which does not differ by an appreciable quantity from the amount the same water at the surface will hold, provided that the concentration of free CO_2 and the temperature be the same in both cases. The increased solubility with depth in the ocean is due entirely to the lower temperature of the water and to the increased proportion of free CO_2 , but not at all to the increased hydrostatic pressure there prevailing.

The only pressure which does affect the solubility is the partial pressure, i.e., the proportion, of CO_2 in the layer of atmosphere³ in

¹ R. A. Daly, *Bull. Geol. Soc. Am.*, XX (1909), 156; also in "Geology of North American Cordillera," *Memoir No. 38, Geol. Survey of Canada*, Part II (1912), p. 651. Italics are ours.

² Increase of hydrostatic pressure *decreases* the solubility of some substances. In any case the effect is very small indeed; its magnitude and direction can be calculated if the appropriate data on volume changes are known. Cf. Johnston and Niggli, *Jour. Geol.*, XXI (1913), 504, where references are given.

³ The proportion of CO_2 in the air increases, *ceteris paribus*, as we pass from higher to lower levels; but this is a factor of no moment to the present discussion because the diffusion downward through the water is in all probability very slow in comparison with the natural circulation of the water.

contact with the solution, for there is a definite and quickly attained equilibrium between the proportion of CO_2 in the adjacent atmosphere and the concentration of free CO_2 in the water, the factor of proportionality being the absorption coefficient (the solubility) of CO_2 in the solution at the particular temperature. It is true that water at depth can hold more CO_2 in solution, if it gets hold of it, for in that case bubbles of CO_2 gas cannot form until its virtual pressure just exceeds the hydrostatic pressure; but slow diffusion upward would tend to equalize the concentration at various depths. In the ocean, on the other hand, the content of CO_2 is only what it was able to absorb when at the surface, supplemented by that which has been produced by organic processes—the latter being in all probability but a small fraction of the whole in deep water.¹ However this may be, it is manifest why the water at depth should contain more CO_2 , for its present low temperature, retained from its polar days, establishes the fact that when at the surface in contact with the atmosphere it was cold, and lowering of temperature increases very markedly the amount of CO_2 which water can absorb through contact with an atmosphere containing a constant proportion of CO_2 .² This fact, combined with its present low temperature—for, as we have seen, lowering of temperature of itself increases the solubility of CaCO_3 —suffices to account for the well-known fact that all shells and tests disappear in the depths of the ocean.³

Now let us revert to the consequence of abstraction of CO_2 , and consider what will happen when, in the course of the oceanic circulation, this cold water, which carries more CO_2 and more CaCO_3 than the warmer surface waters,⁴ reaches the surface and is slowly warmed.

¹ Buchanan (*Proc. Roy. Soc.*, XXII [1874], 483) writes: "Down to nearly 2,000 fathoms life is still abundant; below this depth, however, the amount rapidly decreases till, at about 2,800 fathoms, it is, for carbonic acid producing purposes, practically extinct."

² Thus in contact with any atmosphere, water (or a dilute salt solution) absorbs about twice as much CO_2 at 0° as at 20° .

³ See the report of the Challenger expedition or the work of Sir John Murray. In the present connection it is immaterial whether these shells consist of calcite or aragonite, although assertions to the contrary may be found.

⁴ This appears a necessary prerequisite, no matter what be the mechanism of precipitation. Dittmar, in his article in the *Encyclopaedia Britannica*, states that there is a slight but indubitable increase in concentration of calcium with depth. Moreover,

In the first place, it will gradually lose CO_2 to the air, the residual concentration of free CO_2 being dependent at any moment upon the temperature of the water and the proportion¹ of CO_2 in the air at that place. The consequence of this loss is that the amount of calcium in solution will at some point exceed the concentration which the water is able to hold in solution—or, in other words, the product $[\text{Ca}^{++}][\text{CO}_3^{--}]$ reaches its characteristic precipitation value—whereupon precipitation² sets in, and continues thereafter so long as the temperature continues to rise. This process is without doubt taking place now in tropical and subtropical regions wherever and whenever the necessary conditions are fulfilled. It has been correlated³ with the abundant bacterial and planktonic life found under such circumstances, and there would seem to be little question that the organisms are a factor in the process, if only in the sense of catalyzing it. But may it not be, in some cases at least, that the organisms are abundant there because of the abundance of the CO_2 available for their life-processes in such water? For it is to be borne in mind that the precipitation of CaCO_3 is accompanied by the setting free of an equivalent quantity of CO_2 which, if not used up in the sea, will pass into the atmosphere. Be this as it may, the physico-chemical factors are in themselves competent to account for the precipitation⁴ of CaCO_3 on a large scale, and the prerequisite conditions for deposition by this means do not differ materially from the postulates required for precipitation by bacterial action or by organisms generally.

Buchanan (*Proc. Roy. Soc. London*, XXIV [1876]) writes: "There is usually more CO_2 in waters taken from the bottom and intermediate depths than in surface water; but if regard be had to the temperature of the water, it will be seen that there is but little difference in the amount in waters of the same temperature from whatever depth they have been derived." It is to be observed that these determinations all refer to low latitudes; conditions in the Polar regions may well be different.

¹ All experiments indicate that this proportion departs in general very little from 3 parts in 10,000, except in or near large towns. Off the west coast of Greenland, however, amounts up to 7 parts in 10,000 were observed by Krogh (*Meddelelser om Gronland*, XXVI [1904], 409).

² Supersaturation is under these conditions obviously a negligible factor.

³ G. H. Drew, *Carnegie Inst. Publ. No. 182* (1914), p. 7; Kellerman and Smith, *Jour. Wash. Acad. Sci.*, IV (1914), 400. See also recent papers by T. Wayland Vaughan.

⁴ Likewise for its re-solution.

Indeed, there are several facts which point to a parallelism between the amount of lime secreted by organisms and the degree of saturation of the sea with respect to CaCO_3 ; thus the animals of the warm seas secrete more lime, on the average, than the same types in cold seas;¹ and, according to Murray,² "on the whole, lime at the present time appears to be accumulating toward the equator." These observations directly corroborate the idea that solubility is a significant factor even in the secretion of lime by organisms; that the decreasing abundance of calcareous organisms toward the polar regions is a question not only of the decrease of general vitality (rate of growth and of reproduction) with lowering of temperature, but also of the decreasing capacity³ of the organism to secrete CaCO_3 from colder sea-water, this being associated with the fact that, though the concentration of lime is no smaller in the colder water, the degree of unsaturation is greater the colder the sea-water.

According to Murray, "a limited amount of purely inorganic precipitation does, indeed, take place in coral reefs and some shallow water deposits and in the Black Sea."⁴ Now it has been argued⁵ that chemically precipitated limestones are due to the production of ammonia by decaying organic matter; according to this view such limestones could form only when conditions were such that a long-continued process of persistent decay was possible. According to the view emphasized in the present paper—and, be it noted, this is primarily a chemical, rather than a geological, question—chemical

¹ See citations from the *Challenger Reports*, in Chamberlin, *Jour. Geol.*, VII (1899), 576-77.

² *The Depths of the Ocean*, p. 180. "In very deep water, even within the tropics, the calcareous shells do not accumulate on the bottom, being apparently removed through the solvent action of sea-water, and with increasing depth the Globigerina ooze passes gradually into another pelagic type, usually Red Clay" (p. 164). "Pteropod ooze is limited to the tropical and subtropical regions, usually in the neighborhood of oceanic islands and on the summits and sides of submarine elevations; it is found in relatively shallow water, and covers a relatively small extent of the ocean floor" (p. 167).

³ It would be of interest to know if these calcareous organisms could secrete CaCO_3 from colder water kept saturated with calcium carbonate.

⁴ *The Depths of the Ocean*, p. 178.

⁵ Most recently by R. A. Daly, *Bull. Geol. Soc. Am.*, XX (1909), 153; in more extended form in *Memoir No. 38, Geol. Survey Canada* (1912), pp. 643 f.

precipitation would take place wherever, and so long as, a current of water saturated with calcite was being warmed. These views are not at all mutually exclusive; but their implications differ, and it ought to be possible to decide by appropriate observation and deduction in how far either has been a dominant cause on a large scale.

The magnitude of the scale of this presumed process of precipitation through purely inorganic agencies depends primarily upon the rate of circulation and upon the amount of calcium carried by this water rising to the surface. We shall now consider the competence of these agencies as geologic factors. In doing so let us suppose that a cold current of sea-water is not saturated with CaCO_3 until it has reached a temperature of 15° , and that this current after traveling 1,000 kilometers (600 miles) has attained a temperature of 20° ; further, that the water in this stretch of 1,000 km. is changed 10 times a year, corresponding to a current speed of $1,000 \times 10 / 365$ or 27.4 km. a day. Now this water in being warmed from 15° to 20° would precipitate 5.4 parts CaCO_3 per million by weight, or 2 parts per million by volume; on these assumptions,¹ therefore, in the course of a year the mean thickness of the deposit (presuming that all of the precipitate finally settles to the bottom within this stretch) would be $2 / 1,000,000$ of the depth of the current. Hence if the depth of the current is 100 m., the average deposit over the whole area would be, on the specific assumptions just mentioned, 2 mm. yearly.² This estimate is probably a minimum, particularly because we have supposed that deposition would take place over the whole area, whereas in reality deposition would be localized (e.g., if there is, as is likely, a more rapid warming up at some places) so that the deposits actually formed would be thicker. Moreover, the deposit would be redissolved whenever the current is underlain by colder unsaturated water; therefore actual deposits belonging to this category should occur only in localities bathed by currents which are

¹ The numerical values adopted were chosen as being reasonable; in any case these calculations will serve as an illustration, and anyone may make similar calculations using whatever numerical values he deems most consonant with the facts.

² This corresponds to about 5,000 tons CaCO_3 per square kilometer per year, or to a thickness of about 8 inches in a century.

warm and hence comparatively shallow and rising in temperature as they proceed. Consequently, if deposits of CaCO_3 are being formed in this way—and there is no direct evidence at hand which contradicts this view—it should be possible to correlate the position and rate of formation of such precipitated deposits with other things by means of series of bathymetrical observations on the manner of flow of the currents, the temperature of the water, and, above all, the concentration of free CO_2 . As regards the latter, it may be said that the methods hitherto in vogue are very faulty indeed,¹ and that systematic, accurate determinations of the free CO_2 (which can be made by proper choice of method) are very much to be desired, not only on account of their bearing on the present question, but because an accurate knowledge of the concentration of free CO_2 is of high importance² in connection with many biological problems, both theoretical and practical.

Nor would the establishment of this presumed correlation between deposits of CaCO_3 and the physico-chemical conditions prevailing in the ocean be of importance only in relation to present-day formations belonging to this category; it would also be of use in interpreting past deposits of this character which have persisted and in co-ordinating them with other factors. For the rate of formation of such deposits (including the limiting case of zero rate) depends obviously upon the mode and rate of circulation of the ocean and the amount of calcium carried by the water rising to the surface, secondarily, therefore, upon the amount of calcium carbonate brought down by the rivers to the sea; all of which depend ultimately upon the physiographic and petrologic character of the land surface, upon the magnitude of the seasonal variations and regional differences, upon the climate over the whole earth, and upon the proportion of CO_2 in the atmosphere. It would lead too far to discuss this question in all its bearings;³ in order to show the importance of the

¹ See Johnston, *Jour. Am. Chem. Soc.*, XXXVIII (1916), 947.

² The free and combined CO_2 and the alkalinity of the solution are not independent variables, a fact often forgotten; and doubtless many effects ascribed to a change in alkalinity are due equally, or primarily, to a change in the CO_2 equilibrium in the solution.

³ The discussions of Chamberlin (*Jour. Geol.*, VII [1899], 545, 667, 757), Tolman (*ibid.*, p. 585), Krogh (*Meddelelser om Gronland*, XXVII [1904], 334), and others, require some revision in the light of data available since that time.

last factor—apart altogether from the influence of CO_2 as an agency disintegrating the rocks—we have calculated the concentration of the free and combined CO_2 in sea-water at three temperatures for several proportions of CO_2 in the atmosphere. The specific assumptions made in these calculations are: (a) that the molar absorption coefficient (c) of CO_2 is the same as in a 0.6 N (3.5 per cent) solution of sodium chloride; (b) that the water is always saturated with respect to calcite, so that we are justified in using the solubility-product constant (K'_c) corresponding to the temperature; (c) that the degree of ionization of the carbonate is 0.6, a value which is probably high rather than low.¹ On this basis the formula becomes

$$A = \text{total CO}_2 = cP + \sqrt{11200cK'_cP}/0.6,$$

where the first term represents the free CO_2 and the second the total combined CO_2 , each expressed in moles per liter; whence by multiplication by the factor 0.044 one obtains the result in grams CO_2 per cubic meter (parts per million) as given in Table III.

TABLE III

THE CONCENTRATION OF FREE (f), COMBINED (b), AND TOTAL (A) CO_2 —EXPRESSED IN GRAMS CO_2 PER CUBIC METER (PARTS PER MILLION)—IN SEA-WATER AT SEVERAL TEMPERATURES AND SEVERAL PARTIAL PRESSURES (P) OF CO_2 IN THE ATMOSPHERE; CALCULATED ON THE BASIS OF THE SPECIFIC ASSUMPTIONS MENTIONED ABOVE

CO ₂ IN ADJACENT ATMOSPHERE AS		10° $c = 0.0463$ $K'_c = 1.06 \times 10^{-8}$			20° $c = 0.0335$ $K'_c = 0.93 \times 10^{-8}$			30° $c = 0.0260$ $K'_c = 0.81 \times 10^{-8}$		
Parts per 10,000	Partial Pressure P	f	b	A	f	b	A	f	b	A
2.5	0.00025	0.51	81.5	82	0.37	70.0	70	0.29	61.5	62
3.0	.0003	0.61	86.6	87	0.44	74.5	75	0.34	65.5	66
3.5	.00035	0.71	91.1	92	0.51	78.3	79	0.40	68.8	69
30.0	.003	6.12	187.6	193	4.4	160.3	165	3.43	140.8	144
300.0	0.03	61.2	402.	463	44.0	345.	389	34.3	303.	337

The figures for total CO_2 , derived in this way, are in substantial agreement with the results of analyses of sea-water; in any case the

¹ Murray and Hiort (*The Depths of the Ocean* [1912], p. 175) estimate the aggregate degree of ionization in sea-water to be 0.9; but this is undoubtedly much too high.

relative values for the different conditions are probably good even if the absolute values are inaccurate. According to the table, the concentration of total CO_2 in water at constant temperature varies practically as the cube root of P , for the small values of P ; in other words, a change of 3 per cent in the present proportion of CO_2 (e.g., from 3.1 to 3.0 parts per 10,000) will produce a change of but 1 per cent in the concentration of total CO_2 in the sea-water. Likewise under present conditions (i.e., $P=0.0003$) the total CO_2 in the ocean decreases about 1.5 per cent of its value for each degree of rise in temperature. At the higher pressures of CO_2 the proportion of free CO_2 in the water becomes relatively much more important; but a hundred-fold increase in the proportion in the adjacent air would cause only a fivefold increase in the total CO_2 in the sea. In this estimate and in the subsequent discussion, be it noted, the assumption is implicit that the water is continuously saturated with CaCO_3 at 15° for all values of P , which in turn implies that conditions were such that the rivers transported to the sea sufficient lime to achieve this. On this basis, therefore, if the present amount of CO_2 in the atmosphere were increased a hundred fold, the total amount of CO_2 in atmosphere and ocean would be only six times as much as it is now; the conditions of equilibrium always being such that a change in the proportion of CO_2 in the atmosphere is minimized, not through a permanent change in the proportion of free CO_2 in the sea (and of its alkalinity), but ultimately by means of the precipitation or solution of a definite quantity of CaCO_3 .

Let us now make a computation of the ratio of the total amount of CO_2 in the whole ocean to that in the whole atmosphere, this being, of course, a measure of the capacity of the ocean to regulate the proportion now present in the atmosphere. We assume again that the ocean as a whole would be saturated with CaCO_3 if its temperature were 15° ,¹ and that its mean depth is 3,600 meters;² on this basis the mean amount of CO_2 under each square meter of surface of the sea is $81 \times 3,600$ gm. or 290 kg. The mean amount above each square

¹ This is just equivalent to the assumption that the average proportion of CaCO_3 throughout the ocean is that which corresponds to its solubility at 15° , about 60-70 parts CaCO_3 per million for values of P not far removed from 0.0003. Cf. Table I.

² See *Encycl. Brit.*, article "Ocean."

meter of the earth's surface (sea and land together) is 3 kg.; for if the proportion of CO_2 in the air at the earth's surface is 3 parts per 10,000, the proportion in the whole atmosphere is 2 in 10,000 by volume, hence 3 in 10,000 by weight, or 3 kg. per square meter. Consequently, since the ocean covers about 71 per cent of the total surface of the globe, the ratio

$$\frac{\text{total CO}_2 \text{ in ocean}}{\text{total CO}_2 \text{ in air}} = \frac{290 \times 0.71}{3} = 69.$$

In other words, the ocean contains about 70 times¹ as much CO_2 as the air, on the basis of the assumptions specified above. On this basis the total CO_2 now present in the ocean and atmosphere combined would form a layer of CaCO_3 only about 17 cm. thick over the whole globe, or about 86 cm. (nearly 3 feet) over one-half the present land area; likewise if the amount of CO_2 in the atmosphere were 100 times as much as at present, the corresponding values would be slightly more than 6 times as large, namely, 110 cm. over the globe, or 550 cm. (18 feet) over one-half the present land area. The possible deductions, however, must remain uncertain until series of simultaneous accurate determinations of free and total CO_2 , temperature, and salinity in the sea at various depths and in different localities shall have been made.

The precipitation of CaCO_3 in forms other than calcite.—Besides calcite, which is the stable crystalline form of CaCO_3 under all ordinary conditions, there are two unstable crystalline forms, aragonite and $\mu\text{-CaCO}_3$, which may precipitate under certain circumstances. This whole question is discussed at length in another paper, to which the reader desirous of further information is referred;² we shall here merely recapitulate the conclusions relevant to the present discussion. The existence of the μ -form in nature has not been definitely established, possibly by reason of the fact that some of the criteria which have been used to differentiate the several forms of CaCO_3 have not been unexceptionable, possibly on account of its

¹ This estimate is higher than that (27 times) of Krogh (*Meddelelser om Gronland*, XXVI [1904], 420) or that (55 times) given in Chamberlin and Salisbury's *Geology*, II, 661, which see, with respect to the whole discussion.

² "The Several Forms of Calcium Carbonate," Johnston, Merwin, and Williamson, *Am. Jour. Sci.* (4), XLI (1916), 473.

instability, for in presence of water the μ -form transforms to calcite in a few days. Calcite also appears as spherulites and as "amorphous" CaCO_3 ; but there is little question that the divergent properties of the latter are due entirely to its fineness of grain, i.e., to its extent of surface in proportion to its mass. Consequently the only form other than calcite which we need consider here is aragonite.

Apparently aragonite is formed in nature (*a*) through organic agencies (e.g., in certain shells), (*b*) by deposition from hot springs, (*c*) when an isomorphous carbonate is present to serve as nucleus, and (*d*) by chemical precipitation in saline waters, even at ordinary temperatures, under circumstances which we are unable to specify except by saying that the presence of sulphate appears to be a favorable factor. But *pure* aragonite cannot persist for any length of time in presence of water and calcite, hence only in special circumstances will it be found persisting in the sea. There is, however, the possibility that aragonite may take up in solid solution enough material to bring its own solubility below that of calcite, and hence in the saline solution in equilibrium with the solid solution to render the latter stable with respect to calcite; on this basis it is possible that such impure aragonite may persist in contact with sea-water under certain circumstances, although when exposed to the action of meteoric waters it would soon transform to calcite. However this may be, the circumstance that CaCO_3 precipitates otherwise than as calcite would not of itself affect appreciably anything stated in this paper, since the whole effect would be that ensuing upon the substitution for the solubility-product constant of calcite of the corresponding value for the other form, the latter being certainly no more than twice as great as the former; so the precipitation of the less stable forms is therefore of only subsidiary importance in the present connection.

Summary.—Though organic agencies are predominantly responsible for the deposition of calcium carbonate, yet the purely inorganic factors should also be taken into account in discussions of the mode of deposition. In this paper emphasis has been laid on one point which has not received adequate recognition; namely, the concentration of calcium relative to the limiting saturation concentration of calcium carbonate under the particular conditions, or, in other

words, the relative degree of saturation with respect to calcium carbonate in the ocean. The importance of this factor is obvious if we recollect that the chance of a permanent deposit is, *ceteris paribus*, greater the more nearly saturated the surrounding water is; its neglect is doubtless due to the erroneous and misleading statements as to the solubility of CaCO_3 which have been prevalent. The solubility under specified conditions can now be calculated with the requisite accuracy; it is affected materially by variations of temperature and of concentration of free CO_2 such as occur in nature. For example, a change in the proportion of CO_2 in the adjacent air from 3.2 to 3.0 parts per 10,000, or an increase of temperature of 2°C . would result ultimately in the precipitation of about 2 gm. CaCO_3 from every cubic meter of a solution saturated with it. Comparison of the solubility as calculated with the available analytical data indicates that the warmer surface layers of the sea are substantially saturated with respect to calcite, and consequently that precipitation is to be expected wherever the water is being warmed or is losing CO_2 , or both, and this independently of any other agencies. Indeed, these inorganic factors must be considered no matter what may be the agency inducing precipitation; for example, there is ground for believing that calcareous organisms are more abundant the more nearly saturated with CaCO_3 the water is. The view here advocated, that a somewhat greater rôle be assigned to the inorganic factors than has hitherto been usual, does not conflict with other views—it merely shifts the emphasis a little; nor does it conflict with any facts that have been definitely ascertained. Its precise importance can be determined only by accurate determination of temperature, salinity, and particularly of concentration of CO_2 —free and total—of the water carried out systematically over the ocean; the results of such an investigation, properly carried out, would have an important bearing on many outstanding biological, as well as geological, problems.